

Biopolymer Solutions and Gels: Structural and Thermodynamic Properties

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Study of the thermodynamic and structural aspects of ion/polymer interactions has the potential to contribute to a more comprehensive understanding of the mechanism of ion-mediated structural organization of charged biopolymer systems. The basic physical feature that governs the swelling properties of aqueous polyelectrolyte gels is the competition between ionic (Coulomb) interactions of charged units and nonionic (hydrophobic) interactions of neutral units. In particular, it is known that in hydrogels the electrostatic/hydrophobic interplay can lead to a volume transition. We compared the effect of ions on the osmotic and scattering behavior of a biological and a synthetic polyelectrolyte gel: DNA and polyacrylic acid. Both gels exhibit a reversible volume transition in near-physiological salt solutions as the concentration of divalent ions (in the present case calcium ions) increases. We studied the competition between monovalent and divalent cations by anomalous small angle X-ray scattering (ASAXS). The ASAXS results reveal that the local concentration of the divalent counter-ions in the vicinity of the polymer chains significantly exceeds that of the monovalent counter-ions. A scattering formalism is proposed to describe ion-exchange induced changes in the gel structure occurring at different length-scales in near-physiological salt solutions.